



IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Group Art Unit: 1712  
Examiner: Jeffrey Robertson

In Re PATENT APPLICATION OF

Applicants : Dieter KERNER et al.

Appln. No. : 10/084,336

Conf. No. : 5608

Filed : February 28, 2002

For : SURFACE-MODIFIED, DOPED,  
PYROGENICALLY PRODUCED  
OXIDES

Atty. Dkt. : 39509-177800

**SUBMISSION OF DECLARATION**  
**UNDER 37 C.F.R. 1.132**

26694  
U.S. PATENT AND TRADEMARK OFFICE

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May 26, 2005

Commissioner for Patents  
P.O. Box 1450  
Alexandria, VA 22313-1450

Sir:

Submitted herewith is a Declaration Under 37 C.F.R. 1.132 for Dr. Jürgen Meyer for the  
above-identified Application.

Respectfully submitted,

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**DECLARATION UNDER 37 C.F.R. 1.132**

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

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In re Application of: Dieter Kerner et al.  
Serial No. 10/084,336  
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Group Art Unit: 1712

Examiner: Robertson, Jeffrey

Commissioner for Patents  
P.O. Box 1450  
Alexandria, VA 22313-1450

Declaration Under 37 C.F.R. 1.132

Dear Sir:

Dr. Jürgen Meyer declares as follows:

1. I am a co-inventor of the subject matter of the above-identified patent application.
2. My qualifications are set forth in Exhibit A.
3. Under my direction and control, the following experiments were performed:

A burner arrangement as described in reference DE 196 50 500 was used.

Example 1

Doping with aerosol produced from a solution of potassium chloride; 4.44 kg/h  $\text{SiCl}_4$  are vaporized at approx. 130 °C and transferred to the central burner tube as described in DE 196 50 500. Hydrogen in the amount of 3.25  $\text{Nm}^3/\text{h}$  as well as 5.25  $\text{Nm}^3/\text{h}$   $x_1$ : air and 0.55  $\text{Nm}^3/\text{h}$  oxygen is fed into the tube.

This gas mixture flows from the inner burner nozzle and flames in the burner chamber of a water-cooled fire tube. To avoid baking on, 0.5  $\text{Nm}^3/\text{h}$  (jacket) hydrogen and 0.2  $\text{Nm}^3/\text{h}$  nitrogen are also fed into the jacket surrounding the main nozzle.

In addition, 40 Nm<sup>3</sup>/h environmental air is sucked into the fire tube under a light negative pressure.

The second gas component fed into the axial tube is an aerosol, produced from a 2.5 % watery potassium chloride (KCl) salt solution. A two-material nozzle in this case functions as aerosol generator having an aerosolizing capacity of 247 g/h aerosol. This watery salt-aerosol is moved through lines heated from the outside by means of 3.5 Nm<sup>3</sup>/h carrier air, leaving the inner nozzle with an exit temperature of 153 °C. The potassium-salt containing aerosol introduced in this way is fed to the flame and correspondingly changes the properties of the generated pyrogenic silicic acid.

Following the flame-hydrolysis, the reaction gases and the resulting pyrogenic silicic acid, doped with potassium (oxide), are suctioned by means of a vacuum through a cooling system and the particle gas flow is cooled in the process to approx. 100 to 160 °C. The solid material is separated from the exhaust gas flow inside a filter or cyclone.

The resulting silicic acid doped with potassium oxide precipitates out in the form of a white powder with fine particles. In a further step, any residual adhering amounts of hydrochloric acid are removed from the doped silicic acid at temperatures ranging from 400 to 700 °C and treatment in water-vapor containing air.

The BET surface of the resulting pyrogenic silicic acid is 107 m<sup>2</sup>/g. The content of the analytically determined potassium oxide is 0.18 % by weight.

All production conditions are shown in Table 1. The flame parameters are shown in Table 2 and all additional analytical data for the resulting silicic acid are shown in Table 3.

#### Example 2

Doping with aerosol produced from a solution of potassium chloride.

The same steps as in Example 1 are taken.

4.44 kg/h  $\text{SiCl}_4$  is vaporized at approx. 130 °C and transferred to the central burner tube as shown in DE 196 50 500. Additionally fed into this tube are 4.7  $\text{Nm}^3/\text{h}$  hydrogen and 5.7  $\text{Nm}^3/\text{h}$  air and 1.15  $\text{Nm}^3/\text{h}$  oxygen. This gas mixture flows from the inner burner nozzle and flames in the burner chamber of a water-cooled fire tube. To avoid baking on, 0.5  $\text{Nm}^3/\text{h}$  (jacket) hydrogen and 0.2  $\text{Nm}^3/\text{h}$  nitrogen are additionally fed into the jacket nozzle surrounding the main nozzle.

In addition, 25  $\text{Nm}^3/\text{h}$  environmental air is sucked into the fire tube under a light negative pressure.

The second gas component fed into the axial tube is an aerosol produced from a 9 % watery potassium chloride salt solution (KCl). A two-material nozzle in this case functions as aerosol generator having an aerosolizing capacity of 197 g/h aerosol. This watery salt-aerosol mixture is moved by means of 4.0  $\text{Nm}^3/\text{h}$  carrier air through lines heated from the outside and exits from the inner nozzle with an exit temperature of 123 °C. The potassium-salt aerosol introduced in this way is fed to the flame and correspondingly changes the properties of the generated pyrogenic silicic acid.

Following the flame-hydrolysis, the reaction gases and the resulting doped pyrogenic silicic acid are suctioned by means of a vacuum through a cooling system and the particle gas flow is cooled in the process to approx. 100 to 160 °C. The solid material is separated from the exhaust gas flow inside a filter or cyclone.

The resulting potassium-oxide doped pyrogenic silicic acid precipitates out in the form of a white powder with fine particles. In a further step, any residual adhering amounts of hydrochloric acid are removed from the doped silicic acid at temperatures ranging from 400 to 700 °C and treatment in water-vapor containing air.

The BET surface of the pyrogenic silicic acid is 127  $\text{m}^2/\text{g}$ .

All production conditions are shown in Table 1. The flame parameters are shown in Table 2 and all additional analytical data for the resulting silicic acid are shown in Table 3.

### Example 3

Doping with an aerosol produced from a solution of potassium chloride; 4.44 kg/h  $\text{SiCl}_4$  is vaporized at approx. 130 °C and transferred to the central burner tube as shown in DE 196 50 500. Additionally fed into this tube are 2.5  $\text{Nm}^3/\text{h}$  hydrogen and 7.0  $\text{Nm}^3/\text{h}$  oxygen. This gas mixture flows from the inner burner nozzle and flames in the burner chamber of a water-cooled fire tube. To avoid baking on, 0.3  $\text{Nm}^3/\text{h}$  (jacket) hydrogen and 0.2  $\text{Nm}^3/\text{h}$  nitrogen are additionally fed into the jacket nozzle surrounding the main nozzle.

In addition, 45  $\text{Nm}^3/\text{h}$  environmental air is sucked into the fire tube under a light negative pressure.

The second gas component fed into the axial tube is an aerosol produced from a 2.48 % watery potassium chloride salt solution (KCl). A two-material nozzle in this case functions as aerosol generator having an aerosolizing capacity of 204 g/h aerosol. This watery salt-aerosol is moved through lines heated from the outside by means of 3.5  $\text{Nm}^3/\text{h}$  carrier air, leaving the inner nozzle with an exit temperature of 160 °C. The potassium-salt containing aerosol, introduced in this way, correspondingly changes the properties of the generated pyrogenic silicic acid.

Following the flame-hydrolysis, the reaction gases and the resulting pyrogenic silicic acid, doped with potassium (oxide), are suctioned by means of a vacuum through a cooling system and the particle gas flow is cooled in the process to approx. 100 to 160 °C. The solid material is separated from the exhaust gas flow inside a filter or cyclone.

The resulting potassium oxide doped pyrogenic silicic acid precipitates out in the form of a white powder with fine particles. In a further step, any residual adhering amounts of hydrochloric acid are removed from the doped silicic acid at temperatures ranging from 400 to 700 °C and treatment in water-vapor containing air.

The BET surface of the resulting pyrogenic silicic acid is 208  $\text{m}^2/\text{g}$ . The content of analytically determined potassium oxide is 0.18 % by weight.

All production conditions are shown in Table 1. The flame parameters are shown in Table 2 and all additional analytical data for the resulting silicic acid are shown in Table 3.

#### Example 4

Doping with an aerosol produced from a solution of potassium chloride; 4.44 kg/h  $\text{SiCl}_4$  is vaporized at approx. 130 °C and transferred to the central burner tube as shown in DE 196 50 500. Additionally fed into this tube are 2.0  $\text{Nm}^3/\text{h}$  hydrogen and 6.7  $\text{Nm}^3/\text{h}$  air. This gas mixture flows from the inner burner nozzle and flames in the burner chamber of a water-cooled fire tube. To avoid baking on, 0.3  $\text{Nm}^3/\text{h}$  (jacket) hydrogen and 0.2  $\text{Nm}^3/\text{h}$  nitrogen are additionally fed into the jacket nozzle surrounding the main nozzle.

In addition, 35  $\text{Nm}^3/\text{h}$  environmental air is sucked into the fire tube under a light negative pressure. The second gas component fed into the axial tube is an aerosol produced from a 2.48 % by weight watery potassium chloride salt solution (KCl). A two-material nozzle in this case functions as aerosol generator having an aerosolizing capacity of 246 g/h aerosol. This watery salt-aerosol is moved through lines heated from the outside by means of 3.5  $\text{Nm}^3/\text{h}$  carrier air, leaving the inner nozzle with an exit temperature of 160 °C. The potassium-salt containing aerosol, introduced in this way, correspondingly changes the properties of the generated pyrogenic silicic acid.

Following the flame-hydrolysis, the reaction gases and the resulting pyrogenic silicic acid, doped with potassium (oxide), are suctioned by means of a vacuum through a cooling system and the particle gas flow is cooled in the process to approx. 100 to 160

The resulting potassium oxide doped pyrogenic silicic acid precipitates out in the form of a white powder with fine particles. In a further step, any residual adhering amounts of hydrochloric acid are removed from the doped silicic acid at temperatures ranging from 400 to 700 °C and treatment in water-vapor containing air.

The BET surface of the resulting pyrogenic silicic acid is 324  $\text{m}^2/\text{g}$ . The content of analytically determined potassium oxide is 0.18 % by weight.

All production conditions are shown in Table 1. The flame parameters are shown in Table 2 and all additional analytical data for the resulting silicic acid are shown in Table 3.

#### Table 1

Experimental conditions for producing doped pyrogenic silicic acid.

No :	SiCl <sub>4</sub> kg/h	primary air Nm <sup>3</sup> /h	added O <sub>2</sub> Nm <sup>3</sup> /h	H <sub>2</sub> core Nm <sup>3</sup> /h	H <sub>2</sub> jack et Nm <sup>3</sup> /h	N <sub>2</sub> jacke t Nm <sup>3</sup> /h	gas tempe r. °C	potassi um salt solutio n KCl weight%	aeros ol amount t g/h	air/aeros ol Nm <sup>3</sup> /h	BET m <sup>2</sup> / g
1	4.44	5.25	0.55	3.25	0.5	0.2	153	2.5	247	3.5	107
2	4.44	5.7	1.15	4.7	0.5	0.2	123	9	195	4	127
3	4.44	7	0	2.5	0.3	0.2	160	2.48	204	3.5	208
4	4.44	6.7	0	2.0	0.3	0.2	139	2.48	246	3.5	324

Explanations: Primary air = amount of air in the central tube; H<sub>2</sub> core = hydrogen in the central tube; gas-temperature = gas temperature at the nozzle for the central tube; aerosol amount = mass flow of the salt solution converted to aerosol; air/aerosol = carrier gas amount (air) of the aerosol

Table 2

Flame parameters during the production of doped pyrogenic silicic acid.

No:	gamma core	lambda core	vk <sub>norm</sub> [m/sec]
1	2.77	1.01	20.8
2	4.00	1.00	25.9
3	2.13	1.17	21.6
4	1.71	1.40	20.0

Explanations: gamma core = hydrogen ratio in central tube; lambda core = oxygen ratio in central tube; for a precise computation and definition of gamma and lambda see EP 0 855 368;  
vk<sub>norm</sub> = outflow speed under normal conditions (273 K, 1 atm)

Table 3

Analytical data for the samples obtained with example 1 and 4

No.	BET [m <sup>2</sup> /g]	pH 4% watery dispersion	potassium content as K <sub>2</sub> O [% by weight]	DEP at 16g weighed portion in [g/100g]	bulk density [g/l]	ramming density [g/l]
1	107	7.07	0.18	k.E.	24	32
2	127	7.71	0.316	k.E.	31	42
3	208	6.66	0.15	234	19	25
4	324	6.35	0.18	305	17	22

Explanations: pH 4% sus. = pH value of the four percent watery suspension; DBP = dibutylphalate absorption; k.E. = equipment did not detect an end point.

## Hydrophobing

### Example 5

A batch of 2.5 kg hydrophilic, potassium [K]-doped silicic acid described in Example 3 is placed into a mixer and, under intensive mixing, is sprayed with a two-material nozzle initially with 0.125 kg water and

subsequently with 0.3 kg hexamethyldisilazane. Following the spraying, the material is mixed for an additional 15 minutes and is subsequently cured at a temperature of 25°C for 5 hours and then at 120°C for 2 hours.

#### Example 6

A batch of 2.5 kg hydrophilic, potassium [K]-doped silicic acid described in Example 4 is placed into a mixer and, under intensive mixing, is sprayed by means of a two-material nozzle initially with 0.125 kg water and subsequently with 0.45 kg hexamethyldisilazane. Following the spraying, the material is mixed for an additional 15 minutes and is subsequently cured at a temperature of 25°C for 5 hours and then at 120°C for 2 hours.

Testing of the inventive hydrophobic, potassium-doped silicic acid in silicone rubber.

Table 4  
Analytical data

	BET surface [m <sup>2</sup> /g]	pH value	K <sub>2</sub> O content [% in weight]	ramming density [g/l]	drying losses [%]
Example 5	163	9.1	0.15	38	0.8
Example 6	232	9.0	0.18	40	1.2

The products shown in Table 4 are tested in a liquid silicone rubber [LSR] formulation. The hydrophilic starting products of aerosol (pyrogenic silicic acid) with comparable surface are used as comparative material.  
LSR silicone rubber

In a planetary-type dissolver, 20% silicic acid is worked in at a slow speed (50/500 min<sup>-1</sup> planetary mixer/dissolver disc) and subsequently dispersed at high speed (100/2000 min<sup>-1</sup>) for 30 minutes.  
The mixture forms a flowable mass with low viscosity following the mixing, wherein the viscosity is somewhat reduced following the thirty-minute dispersion operation.

Owing to the fact that the hydrophilic starting products could be mixed in only in low concentrations or not at all, the Examples 5 and 6 show easy intermingling, an extremely good wettability and also low rheological properties, wherein particularly the yield point as a measure for the



flowability moves toward 0 Pa.

The hydrophilic silicic acids for comparison cannot be worked in at the same concentrations because of the excessive thickening effect (Table 5).

Table 5

Rheological properties for 20% silicic acid

silicic acid	yield point (Pa)	Viscosity D = 10 s <sup>-1</sup> [Pa s]
Example 3*	-	-
Example 4*	-	-
Example 5	0	350
Example 6	0	326

\* = The products cannot be worked in at this concentration (20%) because the thickening effect is too high.

The mixtures are subsequently cross-linked [vulcanized]. In the process, the standard formulation (optimized to a hydrophobic filler material with max. 0.3% drying loss) is changed to the effect that the share of vulcanizing products (catalyst and inhibitor remain unchanged) is increased to match the increase in the drying loss for the hydrophilic filler material used.

Table 6

Mechanical and optical characteristics of the vulcanized products with 20% silicic acid.

silicic acid	tensile strength [N/mm <sup>2</sup> ]	elongation at rupture [%]	resistance to tear propagation [N/mm]	harness [shore A]	bounce-back elasticity [%]	transparence [DE/D65]
Example 5	3.9	244	3	48	62	35
Example 6	4.3	304	21	44	62	53

4. The results of the mechanical and optical tests are combined in Table 6. The extraordinarily high transparence of the mixture according to Example 6 must be emphasized, which cannot be achieved with any other product. These results would have been unexpected. Also surprising and unexpected is the high resistance to tear propagation of the mixture containing the silicic acid

according to the invention.

5. Testing of LSR (liquid silicone rubber) shows that the hydrophobic doped oxides according to examples 5 and 6 show good intermingling and dispersion behavior as compared to aerosols (pyrogenic silicic acids) having identical or similar surfaces and that the compounds have extremely low viscosities and yield points. In particular the extremely high transparency of the vulcanized products is advantageous and unexpected.

6. I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the above-referenced application or any patent issuing thereon.

Date: 04/26/05

  
Dr. Jürgen Meyer